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(71) Applicant

000002118

**Sumitomo Metal Industry Co., Ltd.**

4-5-33, Kitahama, Chuo-ku

Osaka-shi, Osaka-fu

(72) Inventor

**Nobuhiko HIRAIDE**

4-5-33, Kitahama, Chuo-ku

Osaka-shi, Osaka-fu

(72) Inventor

**Hisanobu HASHIZUME**

4-5-33, Kitahama, Chuo-ku

Osaka-shi, Osaka-fu

(72) Inventor

**Yoshio TARUYA**

4-5-33, Kitahama, Chuo-ku

Osaka-shi, Osaka-fu

(74) Agent

**Michio MORI**, Attorney

(with another person)

(54) **[Title of the Invention]**

**HEAT-RESISTANT FERRITE STAINLESS STEEL**

(57) **[Abstract]**

**[Purpose]** To obtain a ferrite stainless steel which has excellent high-temperature strength and thermal fatigue resistance particularly at exhaust gas temperatures of 600 ~ 650°C, oxidation resistance of up to 800°C, excellent workability, corrosion resistance in the weld zone and toughness and is suitable as automobile system member or exhaust gas passage member for LNG/thermal compound power generation.

**[Constitution]** A heat-resistant ferrite stainless steel which consists of, by weight, C: < 0.015%, Si: 0.2 ~ < 0.8%, Mn: 0.2 ~ < 0.8%, P: < 0.03%, S: < 0.002%, Cr: 11 ~ 14%, Ni: < 0.5%, Nb: 0.2 ~ 0.5%, Ti: 0.06 ~ 0.2%, N: < 0.015, Al: 0 ~ 0.2% and, if necessary, one, two or more of Mo: 0.3 ~ 2%, W: 0.1 ~ 1%, V: 0.1 ~ 0.5%, B: 0.0003 ~ < 0.005%, and satisfies  $C+N \leq 0.02\%$ ,  $(Nb+Ti)/(C+N) \geq 20$  and, in case of containing Al,  $Al \geq 2N$ , balance Fe and inevitable impurities.

**[Claims]**

**[Claim 1]** A heat-resistant ferrite stainless steel which consists of, by weight, C: < 0.015%, Si: 0.2 ~ < 0.8%, Mn: 0.2 ~ < 0.8%, P: < 0.03%, S: < 0.002%, Cr: 11 ~ 14%, Ni: < 0.5%, Nb: 0.2 ~ 0.5%, Ti: 0.06 ~ 0.2%, N: < 0.015, Al: 0 ~ 0.2%, and satisfies  $C+N \leq 0.02\%$ ,  $(Nb+Ti)/(C+N) \geq 20$  and, in case of containing Al,  $Al \geq 2N$ , balance Fe and inevitable impurities.

**[Claim 2]** The heat-resistant ferrite stainless steel according to Claim 1 which further contains one, two or more of Mo: 0.3 ~ 2%, W: 0.1 ~ 1%, V: 0.1 ~ 0.5%, B: 0.0003 ~ < 0.005%.

**[Detailed description of the invention]**

**[0001]**

**[Field of industrial application]** The present invention relates to a heat-resistant ferrite stainless steel suitable as an exhaust gas passage member of various internal combustion engines. For

example, it is suitable as automobile system member and exhaust gas passage member for LNG/thermal compound power generation using an exhaust heat recovery boiler.

**[0002]**

**[Prior art]** Exhaust system members such as automobile exhaust manifold, front pipe, center pipe (called automobile exhaust pipes hereafter), etc. are at locations in contact with high-temperature combustion gas exhausted from engines, and various characteristics such as excellent workability, oxidation resistance, high-temperature strength, thermal fatigue resistance, etc. are required for materials constructing the members. However, stainless steel welded pipes have been increasingly used as exhaust system materials in order to respond to demands for recent enhancement of exhaust gas control, rise of exhaust gas temperature caused by improvement of engine performance of automobiles and fuel cost improvement caused by body lightening, etc.

**[0003]** On the other hand, compound power generation using an exhaust heat recovery boiler has recently prospered in thermal power generation plants. The combustion temperature of power generation turbine tends to rise, 1,300°C class, 1350°C class has actually been planned and disposed from prior 1,100°C class, particularly, since LNG is used as a fuel. The exhaust heat recovery boiler for recovering heat of high-temperature exhaust gas on turbine exit side also tends to become the of high-temperature. For example, exhaust gas temperature that was previously around 550°C is increased by about 100°C and becomes around 650°C.

**[0004]** Austenite stainless steels have excellent heat resistance and workability, weldability. SUS304 (18Cr-8Ni), SUS310S (25Cr-20Ni), etc. are cited as a typical species. However, the austenite stainless steel has a large thermal expansion coefficient and is easily damaged due to thermal fatigue caused by heat distortion in use, where severe heat-cooling cycles occur, such as in an automobile exhaust pipe.

**[0005]** The exhaust heat recovery boiler for LNG/thermal compound power generation generally adopts a daytime running-nighttime stop operating mode except for a power consumption peak period, such as mid-summer, etc. Accordingly, if an austenite stainless steel is used in an exhaust heat passage member, e.g., a lined duct, etc., there is a danger of deformation due to heat distortion since the thermal expansion coefficient is large.

[0006] On the other hand, ferrite stainless steel has a smaller thermal expansion coefficient than an austenite stainless steel, and is more favorable when used in an automobile exhaust gas pipe or lined duct, etc. than austenite stainless steel because fatigue failure and deformation caused by heat distortion may be avoided and the price is low.

[0007] Although the ferrite stainless steel is inferior to the austenite stainless steel in the aspect of heat resistance, especially creep strength, as described above, it is said to be suited to structural members for which the creep strength is not so required by best use of the advantages of small thermal expansion coefficient and low price. SUH409L (12Cr-Ti) has heretofore generally been used as heat-resistant ferrite stainless steel. However, a material having more excellent high-temperature strength and creep strength has been desired with the rise of exhaust temperature of automobile exhaust system and exhaust heat recovery boiler.

[0008] Moreover, about 10% of moisture and about 5% of carbon dioxide are contained in an exhaust gas of the exhaust heat recovery boiler for LNG/thermal compound power generation, with regard to the dew point corrosion at the running stop caused by the condensed water, and particularly, corrosion resistance improvement in weld zone has been desired.

[0009] [High-temperature ferrite steel which consists of C: < 0.05%, Si: 1.0 ~ 2.0%, Mn: < 2%, Cr: 6 ~ 25%, Mo: < 5% (however, Cr+Mo  $\geq$  8%), N: < 0.05%, Al: < 0.5%, one or more of Ti, Zr, Ta, Nb (however, C, N of all of Ti, Zr, Ta, Nb are in stoichiometric quantities necessary for carbides and nitrides) and Nb: 0.1 ~ 0.3% (preferably > 0.2%) uncombined (solid-dissolved) Nb and having periodic oxidation resistance and creep strength] is disclosed in Japanese Laid-Open S60-145359.

[0010] It has been mentioned in the same publication that the addition of Si is effective for the periodic oxidation resistance, and the existence of > 0.1 % (preferably > 0.2%) of uncombined (solid-dissolved) Nb and the formation of Laves phase rich in Si is important for creep strength.

[0011] However, the inventors studied the above ferrite steel, consequently, they clarified that a good base material toughness was not easily obtained, the material becomes brittle due to the Laves phase deposition during high-temperature use and there was the danger of being damaged by small impact during cooling when above 1% of Si was contained. Particularly, when a medium-thick plate (plate thickness 3 ~ 9 mm) was used as a structural member, reliability in long-term use was not obtained. A steel disclosed in examples of this invention had such problems that the amounts of Nb,

Ti making a contribution to the stabilization of C, N were small and not enough to prevent the inter-granular attack of a welded heat affected section.

[0012] A ferrite steel excellent in high-temperature oxidation resistance wherein S, O are less than 0.008% and in which inclusion in steel is more stable than MnS at high temperatures has been disclosed in Japanese Laid-Open Patent Application S62-14626.

[0013] The ferrite steel is characterized by the fact that the formation of MnS and oxysulfides of Si, Al, Mn, etc. comprising inclusions exerting an adverse effect on the oxidation resistance is inhibited by decreasing the content of impurities S, O, and it has been described that one, two or more of Ti, Nb, Zr, Ta may be added as C-fixed elements, in total, 4 times as much as the C amount and within a range of 1.5% or less to inhibit the deterioration of oxidation resistance at the time of high-temperature use or by Cr carbide formation.

[0014] However, the impurity N has not been studied and the effect of N on toughness of the base material and welding zone is large, therefore anxiety about the toughness of the welding zone remains. Moreover, studies on effects of the elements on high-temperature strength and thermal fatigue life have not yet been fully made.

[0015] Particularly, when two of Ti, Nb, Zr, Ta being C, N fixed elements are added, a study on a proper amount given by considering the balance of workability, formability, toughness, high-temperature strength and corrosion resistance when Nb and Ti are added by compounding has not yet been made.

[0016]

**[Problems overcome by the invention]** The purpose of present invention aims at obtaining a ferrite steel which has excellent high-temperature strength and thermal fatigue resistance particularly at exhaust gas temperatures of 600 ~ 650°C, oxidation resistance of up to 800°C, excellent workability, corrosion resistance in the weld zone and toughness and is suitable as an automobile system member or exhaust gas passage member for LNG/thermal compound power generation. Moreover, the purpose of present invention is to provide a low-priced ferrite stainless steel of lower cost to the user, e.g., a material making a contribution to the centralization of material which leads to the exhaust manifold-front center pipe-muffler in an automobile exhaust system.

[0017]

**[Problem resolution means]** Automobile exhaust system members generally are 2 mm-thick thin plates or welded pipes, the plate thickness of duct material of exhaust heat recovery boiler is mainly 1.5 ~ 6 mm, and a medium-thick plate of up to about 9 mm is also used. Structurally necessary oxidation resistance, high-temperature strength, thermal fatigue resistance, workability, toughness and weldability are required for all the members. However, the creep strength of common SUS304 and 2.25 Cr-1 Mo ferrite steel is not required, and they should have high-temperature strength endurable to a long-term use because they are members not subjected to strict internal pressure.

**[0018]** Accordingly, the inventors made an earnest study to develop ferrite steel having the above characteristics more excellent than the conventional steel, and consequently obtained the knowledge described below.

**[0019]** A) (Nb, Ti) carbides are formed in case of having a compound addition effect of Nb and an extremely narrow range of 0.006 ~ 0.2% Ti deposit at a higher temperature than carbides in a single addition system of Nb or Ti and are easily deposited with a finely deposited TiN as a nuclei, therefore a region where solid dissolved C, N do not exist (Interstitial Free) is formed at the periphery, by which the steel becomes soft with satisfactory workability and formability, but in sites where the Laves phase preferential deposits decrease simultaneously, there is an effective deposition delay of the Laves phase during high-temperature use and may delay the embrittlement, moreover, the heat distortion is relaxed to improve the thermal fatigue resistance because the re-crystallization temperature is also lowered.

**[0020]** B) The toughness of base material and welding heat affected section is improved and the inter-granular attack of the weld zone in condensed water environment is prevented by controlling the contents so that  $(\text{Nb}+\text{Ti})/(\text{C}+\text{N}) \geq 20$ .

**[0021]** C) The toughness of thermally calendered plate and heat affected section is improved by adopting the Al amount added to improve the oxidation resistance and toughness as  $> 0.02\%$  and  $\text{Al} \geq 2\text{N}$ .

**[0022]** The present invention was accomplished on the basis of such a knowledge. Its substance consists in [A heat-resistant ferrite stainless steel which consists of, by weight, C:  $< 0.015\%$ , Si:  $0.2 \sim < 0.8\%$ , Mn:  $0.2 \sim < 0.8\%$ , P:  $< 0.03\%$ , S:  $< 0.002\%$ , Cr:  $11 \sim 14\%$ , Ni:  $< 0.5\%$ , Nb:

0.2 ~ 0.5%, Ti: 0.06 ~ 0.2%, N: < 0.015, Al: 0 ~ 0.2% and, if necessary, one, two or more of Mo: 0.3 ~ 2%, W: 0.1 ~ 1%, V: 0.1 ~ 0.5%, B: 0.0003 ~ < 0.005%, and satisfies  $C+N \leq 0.02\%$ ,  $(Nb+Ti)/(C+N) \geq 20$  and, in case of containing Al,  $Al \geq 2N$ , balance Fe and inevitable impurities.]

### [0023]

**[Functions]** Next, the contents and functions of alloying components and impurities of the present invention are described.

**[0024]** C & N: An increase of C, N improves the strength but deteriorates the toughness and exerts an adverse effect on workability and weldability. Accordingly, C, N contents are desirably as low as possible, therefore C: < 0.015%, N: < 0.015%, and  $C+N \leq 0.02\%$ . Desirably, C: < 0.01%, N: < 0.010%, and  $C+N$ : < 0.015%.

**[0025]** If  $C+N$  is more than 0.03%, C, N cannot be fixed, an adverse effect appears, and the inter-granular attack susceptibility of weld zone rises even if Ti and Nb are added by compounding.

**[0026]** Si: Si is an effective de-acidifying element necessary for oxidation resistance, and which displays the effect of improving the oxidation resistance by an addition of > 0.2%. Si also has an effect of improving high-temperature strength and thermal fatigue characteristics, because a decrease of solid dissolved Nb making a contribution to high-temperature strength is inhibited and the high-temperature strength is accomplished by substituting a part of Nb with Si in the Laves phase (mainly  $Fe_2Nb$ ) deposited at high temperatures (> 600°C). If >0.8% Si is added, toughness and workability deteriorate, therefore Si must be within a narrow range of 0.2 ~ < 0.8%. Si should desirably be 0.2 ~ 0.6%.

**[0027]** Mn: Mn is a de-acidifying element and is known as an element for improving the hot workability. However, Mn forms MnS to start oxidation and is an austenite forming element, therefore it is undesirable for oxidation resistance. Accordingly, Mn is 0.2 ~ < 0.8%, desirably 0.3 ~ 0.7%.

**[0028]** Cr: Cr is an element necessary for oxidation resistance and corrosion resistance. If Cr is < 11%, its effect does not appear; if it is >14%, toughness and workability deteriorate, therefore the upper limit of the Cr is 14%.

[0029] P: P is an unavoidable impurity in manufacturing, and must be  $< 0.03\%$  to avoid an adverse effect on toughness and workability.

[0030] S: S is also an unavoidable impurity in manufacturing, but if the S amount is large, like Mn, it is undesirable from the viewpoint of oxidation resistance; P also has an adverse effect on weld-ability, therefore the upper limit of S must be  $0.002\%$ .

[0031] Nb: Nb is an element necessary in improving the high-temperature strength and creep strength, weak points of ferrite stainless steels, and the effect markedly appears at  $500^{\circ}\text{C}$  or above. Nb has the function of fixing C, N as carbonitride. In the present invention, Nb is  $0.2 \sim < 0.5\%$  and  $\text{C+N} \leq 0.02\%$ , therefore  $\% \text{Nb}/(\% \text{C} + \% \text{N}) \geq 10$ , ensuring the amount of solid dissolved Nb necessary for obtaining creep strength. The higher the Nb amount, the more desirable from the viewpoint of high-temperature strength, but sufficient high-temperature strength is not obtained at  $< 0.2\%$  and the deposition of the Laves phase becomes remarkable and the toughness deteriorates at  $> 0.5\%$ , therefore Nb is  $0.2\% \sim < 0.5\%$ .

[0032] It was found that the Laves phase ( $\text{Fe}_2\text{Nb}$ ) deposits during high-temperature use ( $> 600^{\circ}\text{C}$ ) and a reduction of high-temperature strength caused by a decrease of amount of solid dissolved Nb occur, but the amount of solid dissolved Nb must be  $> 0.1\%$  to also obtain sufficient high-temperature strength after deposition, therefore the Nb amount must be  $> 0.3\%$ . The lower the Nb amount, the less the deposited amount of the total Laves phase, therefore the upper limit of Nb is  $0.4\%$ .

[0033] Ti: Ti is effective as an element for fixing C, N like Nb. Particularly, it is an element essential to inhibiting the formation of Cr carbide in the welding heat affected section and ensuring the toughness and corrosion resistance. Ti, Nb have the effect of inhibiting the bulking of the crystal grains of the base material and welding heat affected section. The contents must be  $(\text{Nb} + \text{Ti})/(\text{C} + \text{N}) \geq 20$  to fully display these effects.  $(\text{Ti}/\text{Nb})$  is nearly 0.5, and generally may be  $0.2 \sim 1.0$  to further display these effects.

[0034] When Nb and Ti are added by compounding, Ti mainly combines with N to form a nitride, Nb and residual Ti combine with C to form (Nb, Ti) carbide. As described above, (Nb, Ti) carbides deposit at a higher temperature than carbide when only Ti is added and is easily deposited

with fine deposition TiN as nuclei. Accordingly, a region where the solid dissolved C, N does not exist (Interstitial Free) is formed at the periphery.

[0035] Thereby, the steel becomes soft and gives satisfactory workability and formability but sites where the Laves phase preferential deposits are simultaneously reduced, there is an effective deposition delay of the Laves phase during high-temperature use, which may delay embrittlement. Moreover, the heat distortion is relaxed to improve the thermal fatigue resistance because the re-crystallization temperature is also lowered.

[0036] For the purpose of displaying the above effects,  $> 0.06\%$  of Ti must be contained, and its lower limit is an amount which ensures 4 times or more of N and enables forming some carbide. If  $> 0.2\%$  of Ti is added, the above effects are nearly not improved and the surface defects during calendering becomes appreciable, therefore the upper limit is  $0.2\%$ .

[0037] Ni: Ni is an unavoidable impurity in manufacture. The addition of a small quantity of Ni is effective on toughness improvement, but it exerts an adverse effect on the oxidation resistance, therefore it is especially  $< 0.5\%$ .

[0038] Al: Al is an optionally added element and is known as a de-acidifying element, if it coexists with Ti, the effect becomes more appreciable. It is known that toughness is improved by adding a small amount of Al. Particularly, the toughness of hot calendered plate and welding heat affected section is improved by adopting  $2\%N \leq Al$ . Its necessary amount is  $2\%N \leq Al$  to act on the fixing of N with Ti during welding.

[0039] The oxidation resistance is improved by containing  $> 0.02\%$  of Al. Particularly, the peeling resistance of oxide scales is improved and the oxidation resistance is improved by internal oxidation of Al to play a role of "wedge" for scales, inhibiting mixing of oxide scales into the exhaust gas. Moreover,  $> 0.02\%$  of Al also has the effect of improving the high-temperature strength and creep strength. However, an excessive addition saturates the effects on oxidation resistance and high-temperature strength and exerts an adverse effect on workability, therefore the upper limit is  $0.2\%$ .

[0040] Mo: Mo is an optionally added element and is known as an element for improving the high-temperature strength like Nb. Mo is different from Nb, the tendency of forming ( $Fe_2Mo$ ) is smaller than  $Fe_2Nb$  during high-temperature use, and the solid dissolution enhancement action is

lasting because the solid dissolved state is maintained for a long period. Accordingly, the Mo addition is preferable to improve creep strength and corrosion resistance. In this case, these effects are not sufficient at  $< 0.3\%$  Mo, therefore the lower limit is  $0.3\%$ . However, excessive addition reduces the toughness and the workability. In the case of addition, the upper limit is  $2.0\%$  because the cost increases.

[0041] W: W is an optionally added element and is known as an element for improving the high-temperature strength like Nb, Mo. W also has a smaller tendency of forming the Laves phase than Mo, and its solid dissolution action lasts for a longer period, therefore the creep strength is improved. If W is  $< 0.1\%$ , its effects are not enough; if W is excessively added, the toughness and workability deteriorate and the cost increases, therefore W should be  $0.1 \sim 1\%$ .

[0042] V: V is an optionally added element and forms a solid dissolved state or a carbonitride to increase the high-temperature strength and improve the workability. If V is  $> 0.1\%$ , its effects appear. However, if  $> 0.5\%$  is contained, the workability is lowered instead, therefore V should be  $0.1 \sim 0.5\%$ .

[0043] B: B is an optionally added element and is contained with the purpose of improving the high-temperature strength and oxidation resistance.

[0044] Reasons why the improvement effect appear have not been yet been determined, but B is an element that is generally easy to segregate on grain boundary, and hinders the boundary sliding and improves the high-temperature strength. B also discharges impurity elements such as P, S, etc. harmful to oxidation resistance and improves the oxidation resistance by inter-granular segregation. This effect appears at  $> 0.0003$ , if  $> 0.005\%$ , the toughness and workability also deteriorate, therefore B should be  $0.0003 \sim 0.005\%$ .

#### [0045]

[Examples] First, a steel having a composition shown in Table 1 was molten and forged, then hot calendered at a heating temperature of  $1,150^{\circ}\text{C}$ , finished into a  $4.5$  mm-thick plate, and annealed at  $960^{\circ}\text{C}$  to prepare a hot calendered plate. Cold calendering was applied to the  $4.5$  mm-thick calendered plate, the plate is finished and annealed at  $960^{\circ}\text{C}$  to prepare a  $1.5$  mm-thick cold calendered plate. JIS No. 13 ordinary temperature tensile test pieces of  $1.5$  mm in thickness and oxidation test pieces of  $1.5$  mm in thickness,  $20$  mm in width and  $25$  mm in length were sampled in

the T direction from the cold calendered steel plate. Fig. 1 is a diagram showing the shape of a thermal fatigue test piece, **1** is a pipe of test material, 8 mm-diameter holes (**2, 3**) are opened in two places and become feed ports of cooling air. **4** is a holder (grid) from the inner face of pipe. **5** is a mounting part to a holder of a testing machine. The pipe **1** and the holder **4** are fixed with a fixing pin **6** and a weld zone **7**.

**[0047]** Thermal fatigue tests were carried out under a temperature cycle and a mechanical strain waveform shown in Fig. 2 using a computer-controlled electric-hydraulic servo type high-temperature thermal fatigue tester.

**[0048]** The heating of test pieces was carried out by a high-frequency heating equipment and the cooling was carried out by blowing air from the air feed ports to the inner surface of pipe. The test temperature was 200 ~ 800C°, and the constraint condition was 50%.

**[0049]**

[Table 1]

Table 1

Tested Steel		(wt%)								
		C	Si	Mn	P	S	Cr	Ni	Nb	Ti
Invented steel	1	0.008	0.25	0.45	0.021	0.001	12.0	0.12	0.34	0.10
	2	0.008	0.35	0.40	0.019	0.002	11.5	0.11	0.32	0.08
	3	0.007	0.26	0.31	0.016	0.001	12.8	0.08	0.25	0.15
	4	0.006	0.24	0.56	0.015	0.001	13.8	0.20	0.28	0.12
	5	0.006	0.36	0.42	0.018	0.002	11.8	0.26	0.31	0.10
	6	0.009	0.29	0.44	0.025	0.001	12.1	0.12	0.33	0.08
	7	0.008	0.28	0.34	0.015	0.001	11.9	0.09	0.35	0.08
	8	0.007	0.26	0.45	0.019	0.001	12.2	0.16	0.36	0.09
	9	0.009	0.36	0.33	0.018	0.001	11.7	0.07	0.32	0.10
	10	0.009	0.26	0.42	0.021	0.001	11.9	0.21	0.33	0.10
	11	0.007	0.22	0.36	0.019	0.002	12.5	0.17	0.41	0.06
	12	0.010	0.20	0.55	0.015	0.002	13.0	0.18	0.32	0.10
	13	0.008	0.28	0.32	0.025	0.001	12.2	0.15	0.36	0.07
	14	0.011	0.22	0.41	0.028	0.001	11.6	0.08	0.50	0.06
	15	0.007	0.25	0.36	0.021	0.001	12.4	0.12	0.21	0.20
	16	0.008	0.21	0.35	0.020	0.001	11.2	0.06	0.29	0.08
	17	0.007	0.23	0.42	0.019	0.001	11.4	0.08	0.28	0.10
	18	0.009	0.24	0.37	0.021	0.001	11.3	0.10	0.25	0.08
Comparative steel	19	0.010	0.44	0.31	0.022	0.002	11.3	0.09	0.01	0.25
	20	0.010	1.30	0.30	0.022	0.002	11.3	0.20	0.20	0.25
	21	0.015	1.64	0.44	0.020	0.002	12.2	0.06	0.38	0.17
	22	0.012	0.02	0.32	0.022	0.001	11.5	0.12	0.45	0.15
	23	0.009	0.43	0.44	0.021	0.002	11.8	0.23	0.75	0.15
	24	0.011	0.55	0.43	0.018	0.002	12.2	0.19	0.20	0.05
	25	0.008	0.35	0.28	0.019	0.001	11.8	0.11	0.34	0.16
	26	0.015	0.36	0.38	0.020	0.001	12.4	0.08	0.45	0.10
	27	0.010	0.35	0.33	0.024	0.001	13.2	0.10	0.29	0.10

Comparative steel 19 is a steel equivalent to SUH509L    A: (Nb+Ti)/(C+N)    □: beyond a prescribed range of present invention

Table 1 (continued)

Tested Steel		(wt%)								
		Al	N	Mo	W	V	B	(C+N)	A	2×N
Invented steel	1	0.001	0.009	-	-	-	-	0.017	25.9	0.018
	2	0.001	0.006	-	-	-	-	0.014	28.6	0.012
	3	0.001	0.008	-	-	-	-	0.015	26.7	0.016
	4	0.001	0.005	-	-	-	-	0.011	36.4	0.010
	5	0.002	0.006	-	-	-	-	0.012	34.2	0.012
	6	0.025	0.008	-	-	-	-	0.017	24.1	0.016
	7	0.042	0.007	-	-	-	-	0.015	28.7	0.017
	8	0.081	0.008	-	-	-	-	0.015	30.0	0.016
	9	0.021	0.006	1.2	-	-	-	0.015	28.0	0.012
	10	0.001	0.008	-	0.5	-	-	0.017	25.3	0.016
	11	0.001	0.009	-	-	0.25	-	0.016	29.4	0.018
	12	0.001	0.006	-	-	-	0.0005	0.016	26.2	0.012
	13	0.001	0.009	0.8	-	-	0.0007	0.017	25.3	0.018
	14	0.001	0.006	-	-	-	-	0.017	32.9	0.012
	15	0.001	0.006	-	-	-	-	0.013	31.5	0.012
	16	0.024	0.005	0.4	0.8	-	-	0.013	28.5	0.010
	17	0.028	0.006	0.6	-	0.22	0.0003	0.013	29.2	0.012
	18	0.001	0.007	0.3	0.6	0.20	0.0003	0.016	20.6	0.014
Comparative steel	19	0.001	0.009	-	-	-	-	0.019	13.7	0.018
	20	0.050	0.015	-	-	-	-	0.025	18.0	0.030
	21	0.001	0.012	-	-	-	-	0.027	20.4	0.024
	22	0.001	0.011	-	-	-	-	0.023	26.1	0.022
	23	0.001	0.008	-	-	-	-	0.017	52.9	0.016
	24	0.001	0.013	-	-	-	-	0.024	10.4	0.026
	25	0.002	0.001	2.8	-	-	-	0.018	27.8	0.020
	26	0.001	0.001	-	-	-	-	0.025	22.0	0.020
	27	0.022	0.001	-	-	-	-	0.020	19.5	0.020

Comparative steel 19 is a steel equivalent to SUH509L A: (Nb+Ti)/(C+N) □: beyond a prescribed range of present invention

[0050] A hot calendered plate was aged at 600°C for 1,000 hr, JIS No. 4 4 mm-thick Charpy test pieces were sampled in the T direction to evaluate the toughness. Beveling work was applied to the hot calendered plate to butt and TIG weld it under conditions shown in Table 2, and JIS No. 4 4 mm-thick Charpy test pieces were sampled so as to notch it in a welding heat affected section.

[0051]

[Table 2]

**Table 2**

Feeler	410 Nb, diameter 2 mm
Welding current	9- ~ 100 A
Welding voltage	13 V
Welding speed	10 cm/min

[0052] 3 mm-thick plate-like tensile test pieces were sampled from a hot clendered/annealed material and a material given by aging the hot clendered and annealed material at 600°C for 1,000 hr and tests were carried out at 600°C.

[0053] Oxidation tests were carried out at 800°C for 200 hr in air under continuous heating conditions.

[0054] The above various test results are shown in Tables 3, 4. Table 4 shows test results of materials given after the hot calendered plates were annealed and aged. From Table 4, it is known that the invented steels 1 ~ 18 are excellent in workability, high-temperature strength, oxidation resistance and thermal fatigue strength if the ordinary temperature elongation is > 30%, the tensile strength at 600°C is > 25 N/mm<sup>2</sup>, the oxidation gain at 800°C is 2.0 mg/cm<sup>2</sup>, and the thermal fatigue life is 2,000 cycles. It was confirmed that the vTrE of welding heat affected section was below 0°C and the ordinary temperature toughness after aging was also a level at which there was no problem in practice for the invented steels.

[0055] Particularly, as shown by the invented steels 6 ~ 8, it was confirmed that if 0.02 ~ 0.2% of Al was added, the toughness of welding heat affected section was improved. Particularly, it was confirmed that the thermal fatigue strength was improved and the strength lowered after aging was reduced by Mo, W addition with the invented steels 9, 13, 16, 18.

[0056]

[Table 3]

**Table 3**

Tested Steel		Cold Calendered Material			Hot Calendered Material	
		Ordinary temp. elongation (%)	Oxidation gain (mg/cm <sup>2</sup> )	Thermal fatigue life (cycle)	Tensile strength at 600°C (N/mm <sup>2</sup> )	Welding heat affected section vTrE (°C)
Invented steel	1	35	1.5	2,250	30	-15
	2	33	1.2	2,300	31	-10
	3	34	1.1	2,120	27	-12
	4	37	1.4	2,200	29	-18
	5	36	1.3	2,190	28	-16
	6	36	1.2	2,150	29	-18
	7	35	1.0	2,160	29	-20
	8	36	1.0	2,340	31	-22
	9	35	1.2	2,290	32	-5
	10	36	1.4	2,190	29	-8
	11	36	1.8	2,390	32	-11
	12	36	1.5	2,160	29	-10
	13	36	1.3	2,320	31	-7
	14	31	1.6	2,300	31	-1
	15	36	1.5	2,100	26	-15
	16	32	1.3	2,450	31	-6
	17	34	1.5	2,400	31	-5
	18	33	1.6	2,480	32	-7
Comparative steel	19	37	1.4	1,430	20	-5
	20	29	0.7	1,820	22	12
	21	26	0.8	2,230	30	25
	22	34	3.5	2,280	31	-2
	23	25	1.1	2,130	35	28
	24	36	1.2	1,800	22	-18
	25	27	1.0	2,470	34	0
	26	32	1.2	2,060	26	20
	27	35	1.4	2,150	30	10

[0057]

[Table 4]

**Table 4**

		Hot Calendered Material	
		Impact value at 25°C VE <sub>0</sub> (J/cm <sup>2</sup> )	Tensile strength at 600°C (N/mm <sup>2</sup> )
Invented steel	1	56	20
	2	52	21
	3	58	18
	4	60	18
	5	55	17
	6	59	18
	7	62	18
	8	55	20
	9	52	23
	10	53	20
	11	58	21
	12	57	19
	13	55	22
	14	48	21
	15	56	18
	16	55	25
	17	58	25
	18	60	26
Comparative steel	19	250	13
	20	12	13
	21	6	20
	22	71	18
	23	8	20
	24	73	13
	25	52	24
	26	10	18
	27	12	22

[0058] Comparative steel 19 is a steel equivalent to SUH409L, but it is poor in both tensile strength at 600°C and thermal fatigue strength. Comparative steels 20, 24 are poor in both tensile strength at 600°C and thermal fatigue strength because Nb is < 0.2%. Comparative steel 21 is poor in ordinary temperature elongation (<30%) because Si is >0.8% and Comparative steel 25 is poor in workability because Mo is >2%, therefore pipes could not be easily manufactured. Comparative steel

22 is poor in oxidation resistance because Si is  $< 0.2\%$ . Comparative steel 23 is poor in work-ability and toughness of the welding heat affected section, the impact value after aging is low, the embrittlement is appreciable and the strength lowering is also large because Nb is  $> 0.5\%$ .

[0059] Comparative steels 21, 23 have  $vTrE > 0$  and are poor in ordinary temperature toughness after aging because Si is  $< 0.8\%$ .

[0060] Comparative steels 26, 27 are poor in toughness of welding heat affected section because  $C+N \geq 0.02$  and  $(Nb+Ti)/(C+N) \leq 20$ , respectively.

[0061] Moreover, it has been confirmed that no inter-granular attack occurs in the invented steels of  $(Nb+Ti)/(C+N) \geq 20$  by the Straus test of MAG weld zone. However, when  $(Nb+Ti)/(C+N) < 20$  like Comparative steels 1, 2, inter-granular attack cracks in the welding heat affected section were observed.

[0062]

**[Efficacy of the Invention]** Compared with conventional steels such as SUH409, etc., the present invention enables providing a ferrite stainless steel which has excellent high-temperature strength, thermal fatigue characteristic, oxidation resistance, toughness, workability and corrosion resistance in weld zone and is suitable as automobile system member or exhaust gas passage member for LNG/thermal compound power generation.

**[Brief description of the drawing]**

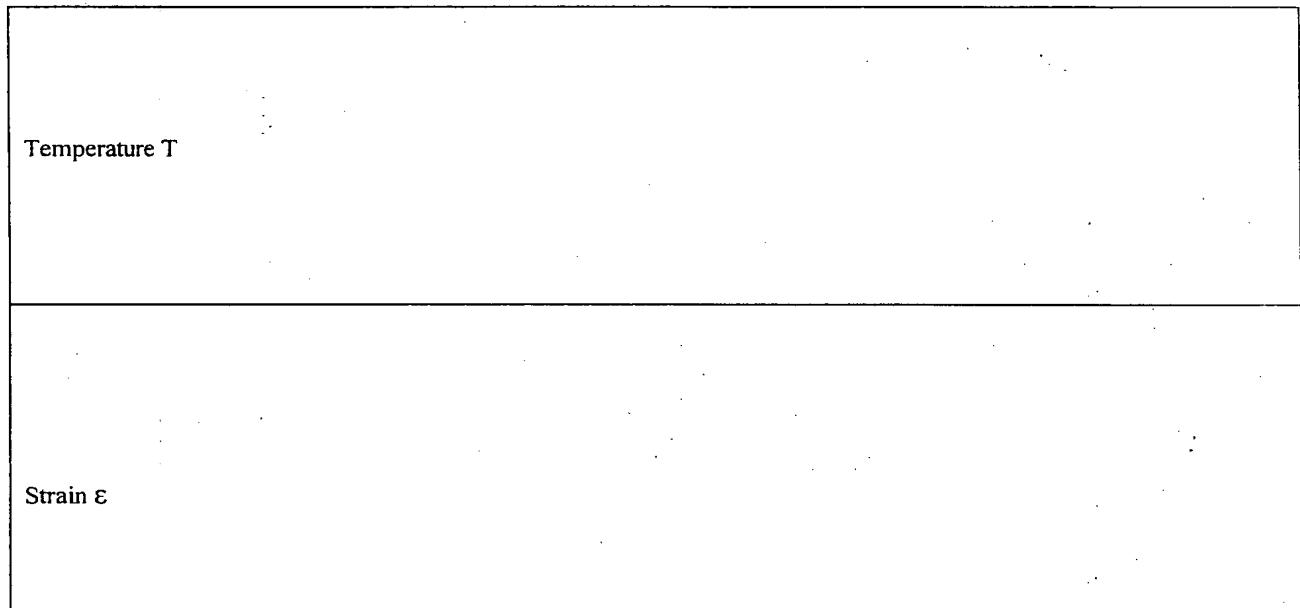
**[Fig. 1]** Diagram showing the shape of a thermal fatigue test piece (gage length: 12 mm).

**[Fig. 2]** Charts showing temperature and strain waveform in thermal fatigue test.

**[Fig. 1]**

- 1 test pipe
- 2 air feed port
- 3 air outlet
- 4 holder
- 5 holder mounting section
- 6 pin fixing hole

**[Fig. 2]**



$\eta$ : degree of constraint

$\alpha$ : coefficient of linear expansion

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|||||  
技術資料  
|||||

## 各種フェライト系ステンレス鋼の耐熱性

中 村 定 幸\* 平 松 直 人\* 清 水 勇\*\* 植 松 美 博\*\*\*

### Heat Resisting Properties of Ferritic Stainless Steels

Sadayuki Nakamura, Naoto Hiramatsu, Isami Shimizu, Yoshihiro Uematsu

#### Synopsis:

Heat resisting properties such as high temperature oxidation, strength, fatigue and thermal fatigue were examined for various ferritic stainless steels. Steels used were NSS 409 M 1, SUS 430, NSS 430 M 3, NSS 442 M3, NSS EM 1 and NSS 444 N, and heat resisting properties were compared among these steels. The effect of alloying elements on heat resisting properties were also studied. The main results obtained are as follows;

- 1) Cr is very effective for improving high temperature oxidation resistance. In this study, NSS EM 1 exhibits the best properties of cyclic and isothermal oxidation resistance.
- 2) Cr, Nb and Mo are effective for improving high temperature strength. The best properties of high temperature strength and high temperature fatigue are obtained for NSS 444 N, followed by NSS EM 1 and NSS 442 M 3.
- 3) The property of thermal fatigue does not rely on its high temperature strength. All ferritic stainless steels exhibit good property of thermal fatigue comparing with austenitic stainless steel of SUS 304. This is due to the fact that ferritic stainless steels have lower thermal expansion than austenitic stainless steels.

#### 1. 緒 言

フェライト系ステンレス鋼は耐食性、加工性に優れ、かつオーステナイト系ステンレス鋼と比較して安価であるため、厨房用、温水器など耐食用途に広く使用されている。しかし、オーステナイト系ステンレス鋼に比べ高温強度が低く、耐熱用構造材料としてはあまり使用されていなかった。

最近、フェライト系ステンレス鋼の高温における表面酸化物の密着性を生かし、自動車排気ガス

浄化装置や各種の燃焼機器などで使用されるようになってきた<sup>1)</sup>。

これらの用途では、耐酸化性は勿論のこと、加熱・冷却にともなう熱応力、機械振動による高温疲労などが問題となる。フェライト系ステンレス鋼は熱膨張が小さく、かつ、熱伝導度が高いためオーステナイト系ステンレス鋼に比べ、優れた熱疲労特性を示す。したがって、フェライト系ステンレス鋼の欠点である高温酸化特性、高温引張り特性および高温疲労特性などの耐熱性を改善すれば、耐熱材料としても有望な鋼種となるものと考え

\*鉄鋼研究所ステンレス・高合金研究部材料第一研究室 \*\*鉄鋼研究所ステンレス・高合金研究部製錬プロセス第3研究室 \*\*\*鉄鋼研究所ステンレス・高合金研究部材料第一研究室長

えられる。

実際に材料を耐熱用として使用する場合には用途によって要求される耐熱特性が異なるため、選択する材料特性を十分に把握しておくことが重要である。しかし、フェライト系ステンレス鋼は耐熱鋼としての歴史が浅いため、系統的な耐熱性に関するデータが少ないのが現状である。

本報告では、汎用的なフェライト系ステンレス鋼である SUS 430 を比較鋼として、耐熱用に使われている代表的なフェライト系ステンレス鋼について高温酸化試験、高温引張試験、熱疲労試験および高温疲労試験を実施し、その特性を系統的にまとめるとともに、金属組織面からの検討を行った。

## 2. 供試材および実験方法

### 2.1. 供試材

表 1 に供試材の化学成分を示す。供試材は 11 % Cr 鋼の NSS 409 M 1 (low C-11 Cr-0.2 Ti)、16 % Cr 鋼の SUS 430、17.5 % Cr 鋼の NSS 430 M 3 (low C-17.5 Cr-0.4 Ti-0.4 Mo) および 19 % Cr 鋼の NSS 442 M 3 (low C-19 Cr-0.5 Cu-0.5 Nb)、NSS EM 1 (low C-1 Mn-19 Cr-0.45 Nb) および NSS 444 N (low C-19 Cr-0.4 Nb-2 Mo) を用いた。

供試材は市販の冷延焼鈍板および半製品の連続铸造スラブを用いた。高温疲労試験片および高温酸化試験片は 2 mm<sup>2</sup> の製品材を用い、高温引張試験および熱疲労試験はスラブ片を用いた。高温引張試験片用にはスラブ片を 25 mm $\phi$  の丸棒に熱間铸造後、NSS 409 M 1 および SUS 430 は 810 $^{\circ}$ C で均熱 6 時間の均質化処理を、NSS 430 M 3、NSS 442 M 3、NSS EM 1 および NSS 444 N は 970 $^{\circ}$ C で均熱 30 分の溶体化処理を行った。熱疲労試験片はスラブ片を 25 mm $\times$ 150 mm $\times$ 1 に熱間铸造後、10 mm<sup>2</sup> まで実験室的に熱間圧延を実施し、NSS 409 M 1、SUS 430 では 810 $^{\circ}$ C で均熱 6 時間の均質化処理を行い、NSS 430 M 3 は 950 $^{\circ}$ C で均熱 3 分、NSS 442 M 3、NSS EM 1 および NSS 444 N は 970 $^{\circ}$ C で均熱 3 分の短時間焼鈍を施した。冷間圧延後、NSS 409 M 1、NSS 430 M 3 は 900 $^{\circ}$ C、SUS 430 は 830 $^{\circ}$ C、また、NSS 442 M 3、NSS EM 1 および NSS 444 N は 950 $^{\circ}$ C でそれぞれ均熱 3 分の短時間仕上げ焼鈍を行った。

各供試材の製品材における物理的性質と機械的性質を表 2 および表 3 に示す。参考のために SUS 304 もあわせて記載した。

### 2.2 試験片および試験条件

図 1 に酸化試験、高温引張試験、高温疲労試験および熱疲労試験に用いた試験片の形状を示す。

表 1 供試材の化学成分 (wt %)  
Table 1 Chemical compositions.

S. No.	C	Si	Mn	Cr	Ti	Nb	Mo	Cu	N	試験項目
NSS 409 M 1	0.011	0.63	0.23	11.08	0.16	—	—	—	0.006	高温疲労, 高温酸化
	0.007	0.39	0.29	10.88	0.38	—	—	—	0.005	高温引張, 熱疲労
SUS 430	0.084	0.55	0.28	16.20	—	—	—	—	0.035	高温疲労, 高温酸化
	0.055	0.64	0.27	16.20	—	—	—	—	0.025	高温引張, 熱疲労
NSS 430 M 3	0.007	0.56	0.26	17.10	0.41	—	0.42	—	0.014	高温疲労, 高温酸化
	0.009	0.50	0.26	17.61	0.28	—	0.40	—	0.012	高温引張, 熱疲労
NSS 442 M 3	0.014	0.52	0.31	18.51	—	0.53	—	0.51	0.012	高温疲労, 高温酸化
	0.014	0.62	0.23	18.72	—	0.46	—	0.54	0.011	高温引張, 熱疲労
NSS EM 1	0.015	0.46	0.85	18.49	—	0.43	—	—	0.016	高温疲労, 高温酸化 高温引張, 熱疲労
NSS 444 N	0.010	0.28	0.32	18.37	—	0.39	1.92	—	0.007	高温疲労, 高温酸化
	0.010	0.24	0.27	18.63	—	0.43	2.00	—	0.012	高温引張, 熱疲労

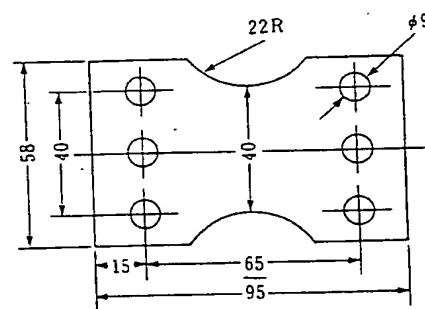
Table 2 Physical properties of various stainless steels.

Table 3 Mechanical properties of various stainless steels at R. T.

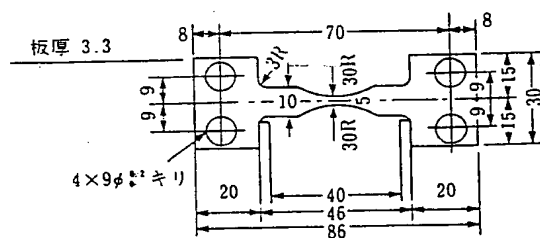
$$\text{重量变化 (mg/cm}^2\text{)} = \frac{W_1 - W_0}{S}$$

$W_0$ : 試驗前重量 (mg)  
 $W_1$ : 試驗後重量 (mg)  
 $S$ : 表面積 (cm<sup>2</sup>)

連続酸化試験には箱型電気炉を用い、アルミナ磁性るつば内に試験片を1枚ずつ入れて炉内に挿入し、所定時間加熱後に炉内より取り出し、スケールが剝離して飛散するのを防ぐため、ルツボ



(c) 高温疲劳試験片



(d) 熱疲労試験片 (単位:mm)

図1 各種試験片の形状および寸法

Fig. 1 Shape and dimension of test samples.

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に蓋をして冷却した。また、繰り返し酸化試験は昇降装置付の堅型管状炉を用い、試験片をフックに吊り下げ、25分間炉内に挿入後、5分間空冷にて50℃以下に下げ、これを1サイクルとし、300サイクルの試験を実施した。

試験後にこぶ状の表面酸化物が発生したもの、あるいは異常に厚い表面酸化物が認められたものは異常酸化と定義した。

高温引張試験片は JIS G 0567 に順じ、直径 10 mm  $\phi$ 、平行部 50 mm のツバ付き試験片を用いた。試験装置はインストロン型の島津精製 IS-10 T 引張試験機に電気炉を装着したものを使用した。試験は 15 分加熱、15 分均熱の後、0.2 % 耐力までを 0.3 %/min、耐力以後は 6 %/min の引張速度にて実施した。

高温疲労試験には板厚 2 mm<sup>1</sup> で中央部に両側 R 22 mm の R 付き試験片を用いた。試験装置はシンク型疲労試験機に電気炉を設置したものを使用した。試験温度は 600℃ および 900℃ で実施し、600℃ では 2500 rpm、900℃ では 3500 rpm の速度による両振り試験を行った。

熱疲労試験には 3.3 mm<sup>1</sup> で中央部に両側 R 30 mm の R 付き試験片を用いた。試験機は直接通電式、完全拘束タイプの熱疲労試験機を用いた。試験条件は昇降温速度が 15℃/sec による 200-900℃ の熱サイクルとし、900℃ にて 30 秒の均熱時間を設定した。破断回数は 2~10 サイクルにおける平均応力の 70 % になった時点での回数とした。

### 3. 実験結果および考察

#### 3.1 高温酸化特性

##### 3.1.1 連続酸化試験結果

図 2 に 900℃ 大気中における連続酸化試験結果を示す。Cr 含有量のもっとも少ない NSS 409 M 1 は短時間で異常酸化を起こし酸化増量が急増している。SUS 430 も 50 時間で酸化増量が急増し、100 時間以内に異常酸化を示した。しかし、Cr 含有量が 17 % 以上の 4 鋼種は 100 時間まで酸化増量は Wagner の放物線則に沿った挙動を示している<sup>2,3)</sup> が、NSS 430 M 3 の酸化増量は NSS 442

M 3, NSS EM 1 および NSS 444 N に比べてやや大きかった。

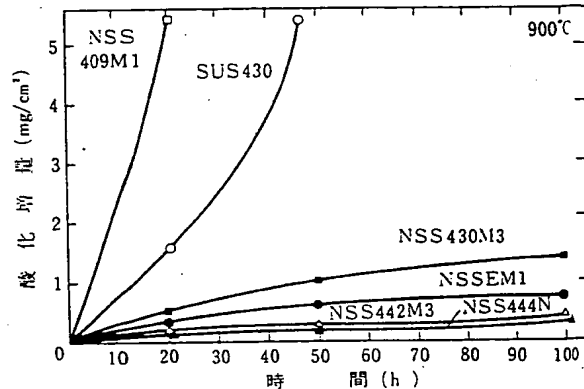


図 2 900℃ 大気中における各種鋼の連続酸化特性  
Fig. 2 Isothermal oxidation of various ferritic stainless steels at 900℃.

図 3 に 1000℃ 大気中における連続酸化試験結果を示す。900℃ とほぼ同様の酸化挙動を示し、NSS 409 M 1 および SUS 430 は短時間で異常酸化を起こすが、18~19 % の Cr を含む NSS 442 M 3, NSS EM 1 および NSS 444 N は放物線則に従った挙動を示す。しかし、Cr 含有量が 17.5 % とやや低い NSS 430 M 3 については 50 時間まで酸化増量が放物線則に従っているものの、100 時間では放物線則よりはずれて酸化増量が大きくなっている。

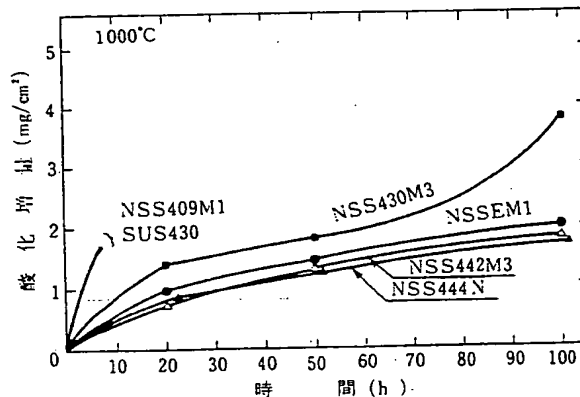


図 3 1000℃ 大気中における各種鋼の連続酸化特性  
Fig. 3 Isothermal oxidation of various ferritic stainless steels at 1000℃.

酸化特性に及ぼす試験温度の影響について、800℃ から 1000℃ までの 100 時間連続酸化試験にて調査した結果を図 4 に示す。NSS 409 M 1 および

SUS 430 については 850℃ を超えると異常酸化するため酸化増量が著しく大きくなっている。また、NSS 430 M 3 は 900℃ を超えると酸化増量がやや増加するが、NSS 442 M 3、NSS 444 N および NSS EM 1 については 1000℃ でも異常酸化を起こさず、1000℃ まで温度の上昇とともに酸化増量がゆるやかに増加している。

写真 1 に 100 時間酸化試験後の表面状態を示す。

800℃ ではいずれの鋼種においても異常酸化は認められないが、900℃ では NSS 409 M 1 および SUS 430 は異常酸化を起こし、厚い酸化物が形成されている。一方、NSS 430 M 3 と NSS 442 M 3 は冷却中に酸化皮膜が剥離している。1000℃ では NSS 409 M 1 と SUS 430 で異常酸化した厚い酸化皮膜が見られる。しかし、NSS 430 M 3、NSS 442 M 3 および NSS 444 N では異常酸化と思われる酸化物は認められないが、いずれも外層の酸化皮膜が剥離しており、密着性が劣っている。NSS EM 1 は 1000℃ においても酸化皮膜の剥離は起きておらず、密着性が良好であることがわかる。

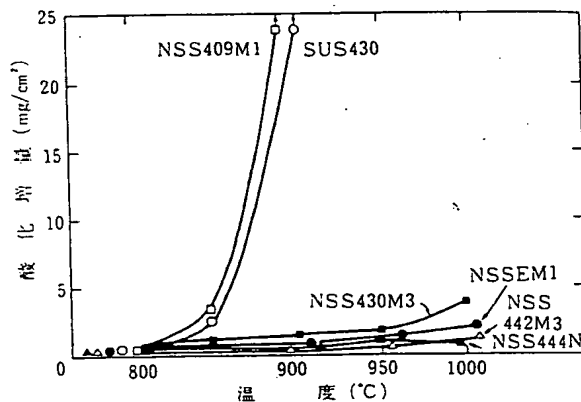


図 4 各種鋼の連続酸化特性に及ぼす試験温度の影響 (試験時間: 100 h)

Fig. 4 Effect of temperature on oxidation properties at temperature between 800°C and 1000°C for 100 h.

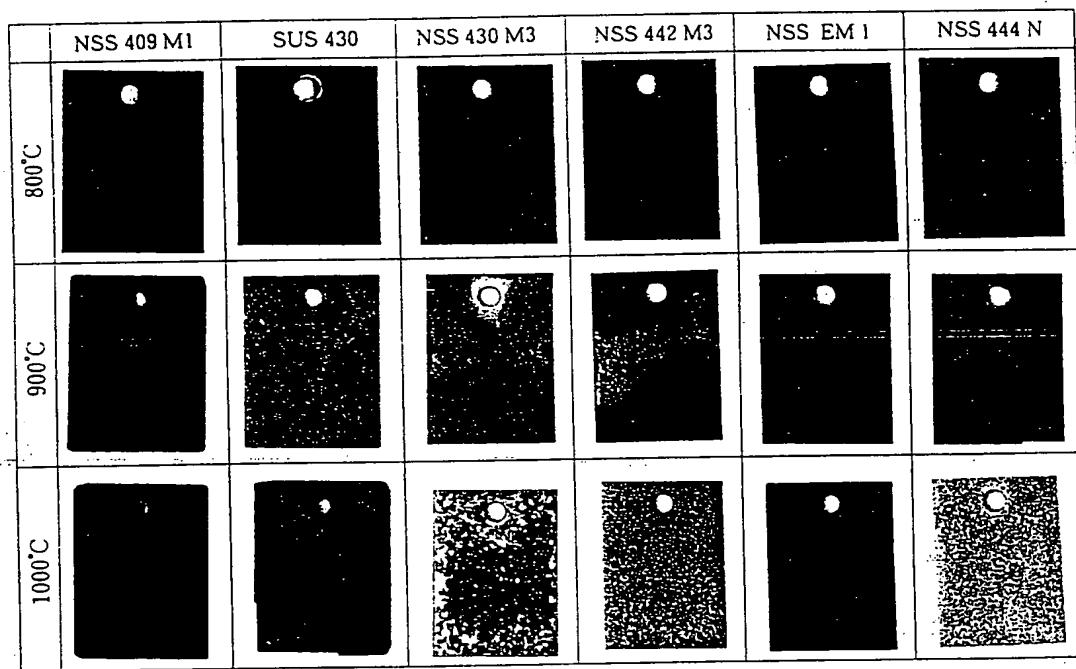


写真 1 大気中連続酸化試験後の各種鋼の外観

Photo. 1 Appearances of steels after isothermal oxidation test for 100 h.

写真2に100時間酸化試験後の断面状態を示す。NSS 430 M 3, NSS 442 M 3, NSS EM1 および NSS 444 N ではいずれの温度においても金属組織変化はないものの, SUS 430 は1000℃において

表層側の粒界に若干内部酸化が見られる。一方, NSS 409 M 1 は900℃ですでに表層部に内部酸化が認められ, 1000℃では異常酸化による極端な板厚減少が見られる。

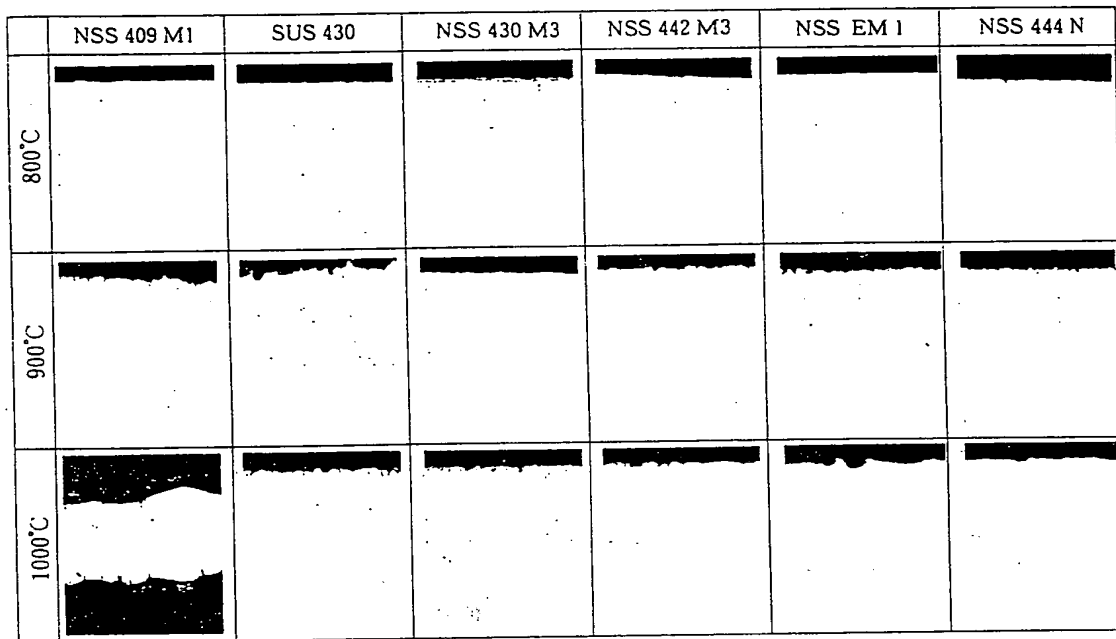


写真2 大気中連続酸化試験後の各種鋼の断面組織

Photo. 2 Optical micrographs of cross section after isothermal oxidation test for 100 h.

100  $\mu$ m

### 3.1.2 繰り返し酸化試験結果

図5に800℃, 900℃および1000℃での繰り返し酸化試験結果を示す。800℃では300サイクル繰返しても酸化増量がほとんどなく, また鋼種間差もない。900℃でも800℃とほとんど大差ないものの, NSS 430 M 3 は200サイクルを超えるとわずかに重量が減少している。

1000℃の結果ではNSS 409 M 1 および SUS 430 は100サイクル以内で異常酸化を起こし, 酸化増量が著しく増加している。他の NSS EM 1, NSS 442 M 3, NSS 444 N および NSS 430 M 3 は50サイクルで重量減となっているが, その中で NSS EM 1 が最も重量変化が少なく, 反対に NSS 430 M 3 の重量変化が最も大きい。NSS 442 M 3 と NSS 444 N についてはほぼ同じ挙動を示し, NSS EM 1 と NSS 430 M 3 のほぼ中間となった。

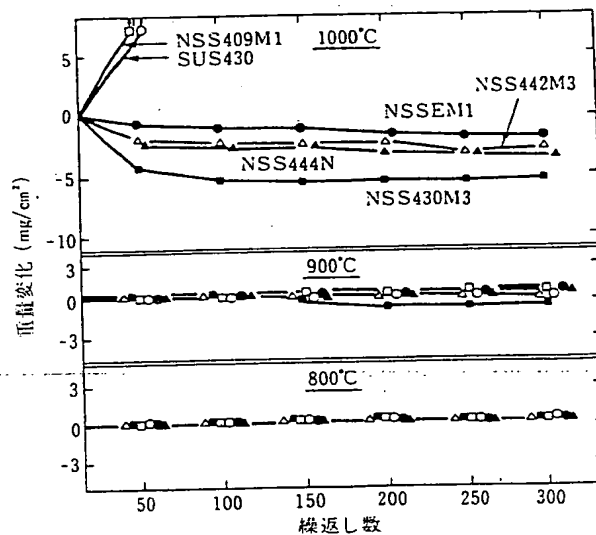


図5 大気中800, 900および1000℃における繰り返し酸化特性

Fig. 5 Cyclic oxidation properties of various ferritic stainless steels at 800°C, 900°C and 1000°C.

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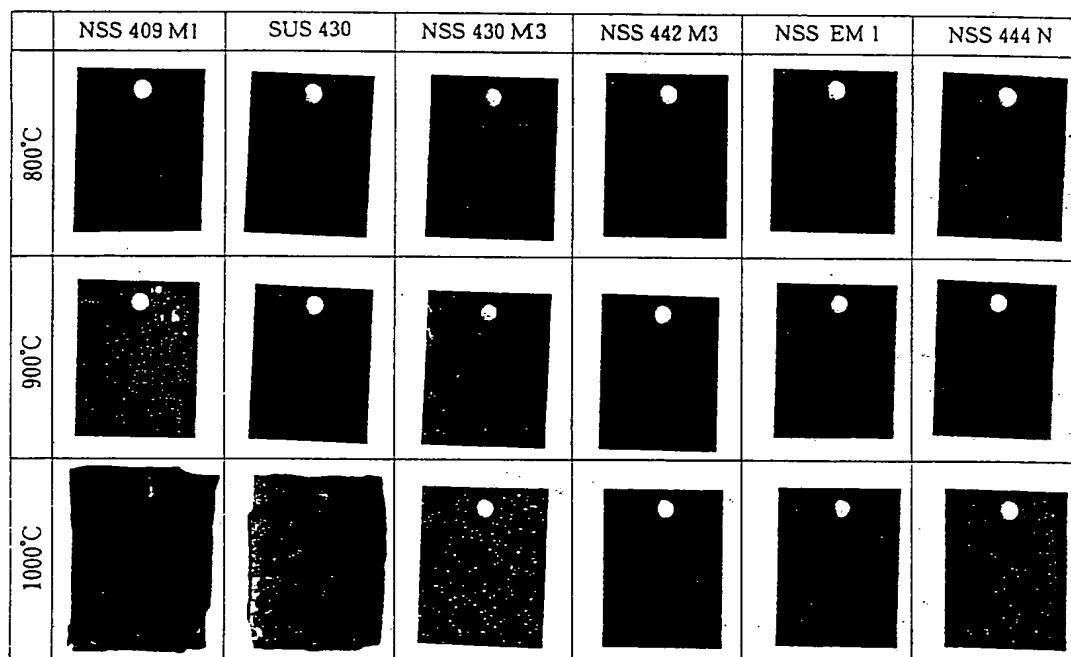


写真3 300 サイクル繰り返し酸化試験後の各種鋼の外観

Photo. 3 Appearances of steels after cyclic oxidation test for 300 cycles.

写真3に300サイクル試験後の外観を示す。800℃ではいずれの鋼種も酸化皮膜の剝離などの欠陥は認められない。900℃ではNSS 409 M1およびNSS 430 M3に若干ではあるが酸化皮膜の剝離が認められる。1000℃になると酸化条件がかなり厳しく、NSS 409 M1およびSUS 430では異常酸化を起こし、非常に厚い酸化皮膜が形成されている。NSS 430 M3、NSS 442 M3およびNSS 444 Nについては異常酸化は起こしていないものの、酸化皮膜の剝離が認められる。これに対し、NSS EM1は酸化皮膜が剝離しておらず、この温度においても良好な酸化特性を示す。

### 3.2 高温引張特性

各鋼種の高温引張試験結果を表4に、0.2%耐力および引張強さを図6に示す。0.2%耐力は温度の上昇とともに徐々に低下する傾向にあるが、その現象は400℃を超えると顕著になる。全体的にNbとMoを含むNSS 444 Nの値が高く、ついでNbを含むNSS 442 M3やNSS EM1が高く、

NSS 409 M1の値が最も低い。このことから、0.2%耐力の上昇はMo、NbおよびCr量の増加と関係しているものと考えられる。

引張強さに関しても0.2%耐力と同様の傾向を示しており、全体的傾向としてNSS 444 Nの値が高く、ついでNSS 442 M3やNSS EM1が高く、NSS 409 M1の値が最も低い。700℃を超えると強度は著しく低下するので、図7に800℃～1000℃の0.2%耐力および引張強さについて詳細に示す。この温度範囲でもNSS 444 Nが最も高い0.2%耐力を示し、NSS 409 M1が最も低い0.2%耐力を示すことから、高温域においてもMo、NbおよびCrが高温強度の改善に対して有効であると考えられる。

引張試験後における伸びおよび絞りの値を図8に示す。伸びに関してはいずれの鋼種とも室温から600℃までは温度の上昇とともにやや低下する傾向にあるが、700℃以上になるとNSS 409 M1、NSS 430 M3およびSUS 430の伸びが増加し、800℃になるとそのほかの鋼種でも伸びが増

加する。900℃から1000℃になると100%以上の伸びを示すものもある。

絞りに関しては室温から600℃までは顕著な傾向は認められず、70~90%の範囲であるが、700℃以上になるとさらに改善され、800℃以上ではいずれの鋼種も高い絞り値を示している。

700℃と900℃の引張試験後の破断部における金属組織を写真4に示す。700℃ではSUS430以外の鋼種では引張試験による歪の影響と思われる引張軸方向の変形組織が認められるが、SUS430では観察されない。NSS409M1、SUS430およびNSS430M3に比べNSS442M3、NSS442M3、NSS442M3およびNSS444Nは粗い展伸状の組織を示している

が、これは引張試験片素材の結晶粒径がやや大きかったことによるものである。900℃ではNSS409M1、SUS430およびNSS430M3に変形後再結晶した組織が認められる。また、約850℃以上でフェライトとオーステナイトの2相となるSUS430はオーステナイト相の析出も観察された。NSS442M3およびNSS442M3は部分的な再結晶組織を示し、NSS444Nは700℃と同様な筋状組織を示している。以上のことから、MoやNbの添加により高温変形後の再結晶が遅くなることを示唆するものと考えられるが、詳細については今後の検討を要する。

表4 高温引張試験結果

Table 4 Tensile properties of various ferritic stainless steels at elevated temperature.

鋼 種	項 目	試 験 温 度								
		R・T	200℃	400℃	500℃	600℃	700℃	800℃	900℃	1000℃
NSS 409 M 1	0.2%耐力 (kgf/mm <sup>2</sup> )	23.4	19.8	22.9	14.2	10.4	7.9	2.9	0.9	0.3
	引張強さ (kgf/mm <sup>2</sup> )	38.7	35.0	29.7	26.2	19.9	10.4	4.0	1.5	0.7
	伸 び (%)	37.6	34.6	29.5	30.0	30.0	59.5	53.8	107.0	124.8
	絞 り (%)	91.5	90.0	88.3	88.5	96.8	≒100	≒100	≒100	≒100
SUS 430	0.2%耐力 (kgf/mm <sup>2</sup> )	28.0	25.5	21.0	20.5	15.0	6.0	3.9	1.2	0.6
	引張強さ (kgf/mm <sup>2</sup> )	48.5	47.6	39.1	38.0	24.1	8.5	6.3	3.1	1.5
	伸 び (%)	32.7	24.8	24.0	22.2	44.2	48.0	54.6	52.3	120.0
	絞 り (%)	70.6	71.9	70.3	60.8	78.0	96.2	≒100	≒100	≒100
NSS 430 M3	0.2%耐力 (kgf/mm <sup>2</sup> )	31.7	22.3	19.1	16.2	13.8	8.8	3.4	1.3	0.5
	引張強さ (kgf/mm <sup>2</sup> )	45.0	38.9	34.4	29.6	21.8	8.9	4.1	2.3	1.0
	伸 び (%)	32.4	32.1	28.6	27.1	34.1	75.4	94.6	90.0	176.1
	絞 り (%)	87.9	62.6	88.0	88.2	93.2	≒100	≒100	≒100	≒100
NSS 442 M3	0.2%耐力 (kgf/mm <sup>2</sup> )	36.0	25.9	27.0	20.5	15.0	10.9	3.3	1.3	0.7
	引張強さ (kgf/mm <sup>2</sup> )	51.5	41.2	42.5	32.0	24.5	17.8	5.3	2.3	1.3
	伸 び (%)	24.2	29.4	22.0	22.2	23.1	23.1	97.9	169.6	157.6
	絞 り (%)	77.0	82.1	71.0	71.3	75.0	84.9	≒100	≒100	≒100
NSS 442 M1	0.2%耐力 (kgf/mm <sup>2</sup> )	28.1	22.7	18.1	16.9	15.0	12.1	4.4	1.6	0.9
	引張強さ (kgf/mm <sup>2</sup> )	44.5	39.2	36.6	32.4	26.5	16.8	5.3	2.6	1.3
	伸 び (%)	33.4	30.9	28.5	26.6	24.1	22.6	92.4	71.1	158.2
	絞 り (%)	76.8	80.9	97.5	93.1	76.7	85.1	≒100	≒100	≒100
NSS 444 N	0.2%耐力 (kgf/mm <sup>2</sup> )	35.4	24.0	26.9	26.4	23.1	17.1	7.9	1.9	0.9
	引張強さ (kgf/mm <sup>2</sup> )	51.6	43.8	43.9	41.4	33.3	20.7	8.9	3.5	1.7
	伸 び (%)	30.7	29.3	26.2	23.0	21.5	22.8	58.3	122.9	154.0
	絞 り (%)	69.6	80.7	76.4	81.0	85.2	91.1	≒100	≒100	≒100

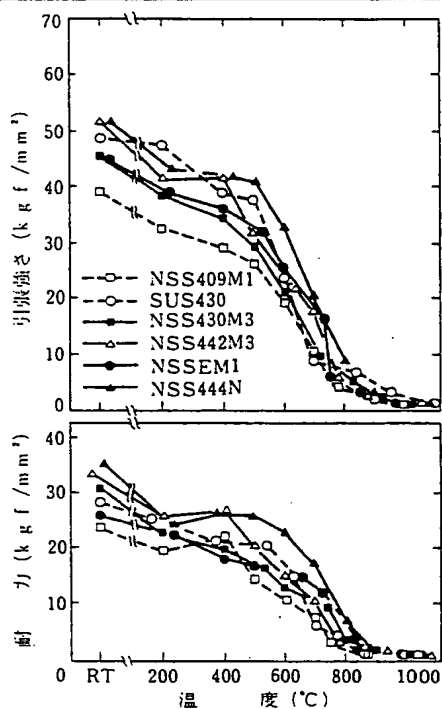


図6 各種鋼の高温引張試験結果

Fig. 6 0.2% proof stress and tensile strength of various ferritic stainless steels at elevated temperature.

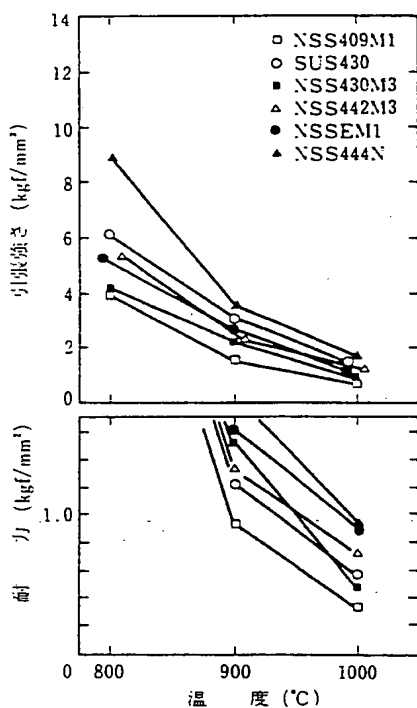


図7 各種鋼の高温引張試験結果 (試験温度 800~1000 °C)  
Fig. 7 0.2% proof stress and tensile strength of various ferritic stainless steels at temperature between 800 °C and 1000 °C

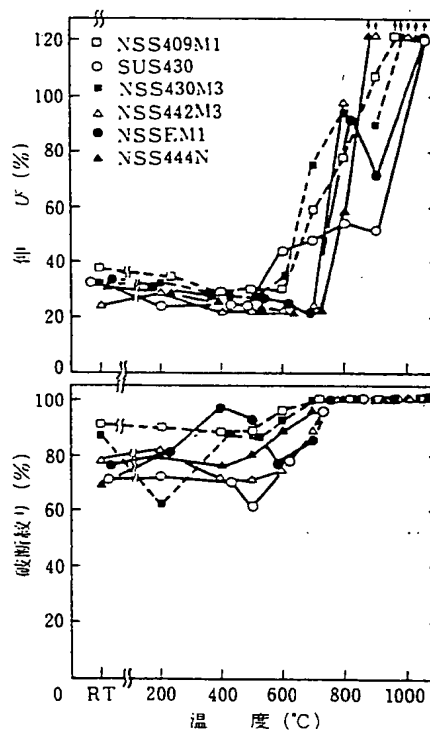


図8 高温引張による各種鋼の伸びおよび断面収り  
Fig. 8 Reduction and elongation of various ferritic stainless steels at elevated temperature.

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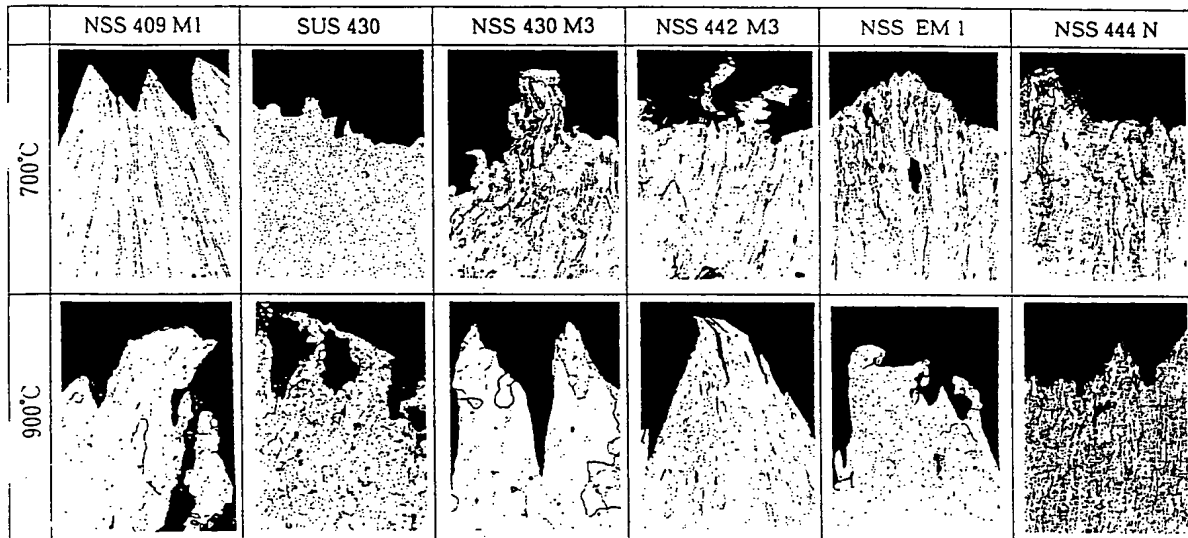


写真4 高温引張試験による破断部の金属組織

Photo. 4 Cracks on cross sections after tensile test at elevated temperature.

50 μm

### 3.3 高温疲労試験結果

#### 3.3.1 600℃における高温疲労試験結果

図9に600℃における高温疲労試験結果を示す。参考のためにオーステナイト系の代表鋼であるSUS 304の結果もあわせて図示した。破損繰返し数が $10^7$ 回以上になる応力を疲労限界応力として比較すると、11% Cr 鋼のNSS 409 M 1が最も低い値を示し、ついでSUS 430, NSS 442 M 3,

NSS EM1, NSS 430 M 3の順に後者ほど高くなり、NSS 444 Nは供試材の中で最も高い疲労限界応力となり、SUS 304と同等の値を示した。一方、この疲労限界応力を同一温度の引張り強度と比較すると、いずれの鋼種も疲労限界応力の方が低い値を示した。

写真5に試験後の金属組織観察結果を示す。いずれの鋼種も試験前と比較して組織あるいは結晶粒径の変化は観察されなかった。

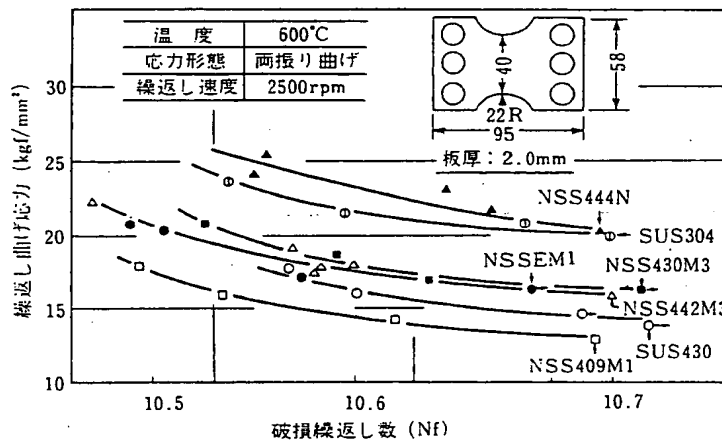


図9 600℃における各種鋼の疲労特性

Fig. 9 Fatigue strength of various stainless steels at 600℃.

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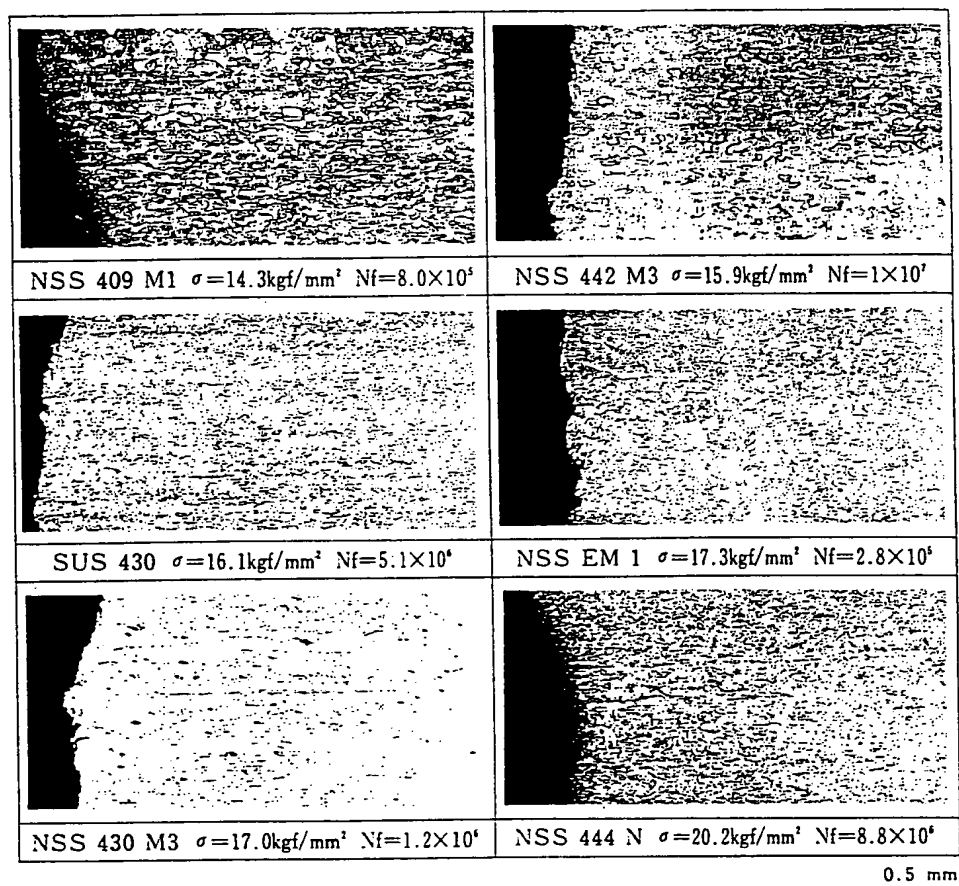


写真5 600℃における疲労試験後の金属組織

Photo. 5 Cracks on cross sections of after fatigue test at 600℃.

## 3.3.2 900℃における高温疲労試験結果

図10に900℃における高温疲労試験結果を示す。疲労限界応力を600℃の試験結果と比較すると、いずれも著しい強度低下が認められる。鋼種間で疲労限界応力を比較すると、600℃と同様NSS444Nが最も高い値を示し、ついでNSS430M3となり、NSS409M1が最も低い値を示した。NSS442M3、NSS EM1およびSUS430はほぼ同じ値で、NSS430M3とNSS409M1の間に位置する。この結果を600℃と同様に同一温度の引張り強度と比較すると、NSS409M1、SUS430、NSS442M3およびNSS EM1はほぼ同じ値を示すが、NSS444NおよびNSS430M3は900℃の引張り強度に対し、疲労限界応力は約2倍の値を示した。

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写真6に試験後の金属組織観察結果を示す。

NSS442M3、NSS EM1、NSS444Nは600℃と同様に金属組織および結晶粒径の変化は認められなかったが、NSS409M1、NSS430M3では結晶粒の粗大化が認められる。一方、SUS430は結晶粒径の成長は認められないが、マルテンサイト相の析出が観察される。900℃におけるNSS444NとNSS430M3の疲労限界応力が引張り強度を越える理由については、ひずみ速度の違いなどが考えられるが、この点については今後の検討が必要である。

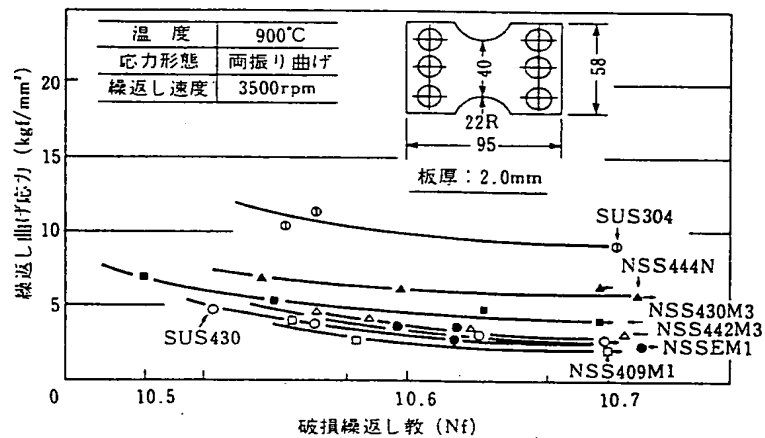


図10 900℃における各種鋼の疲労特性

Fig. 10 Fatigue strength of various stainless steels at 900 °C.

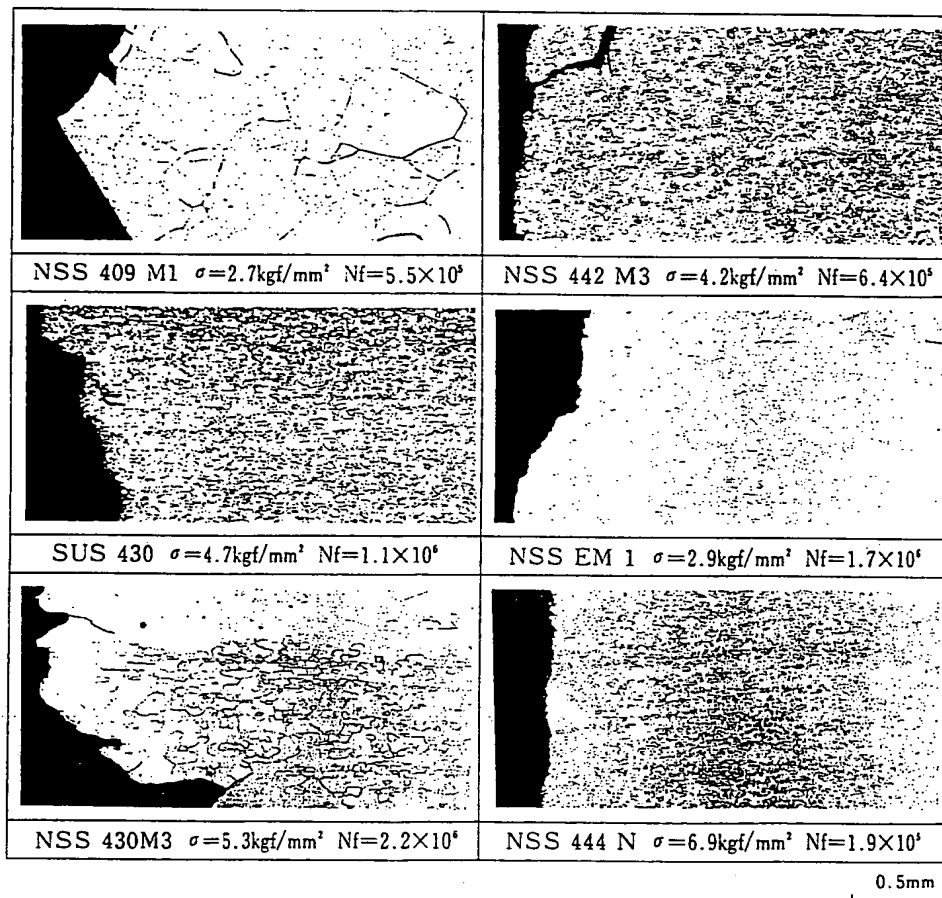


写真6 900℃における疲労試験後の金属組織

Photo.6 Cracks on cross sections of after fatigue test at 900 °C.

## 3.4 熱疲労特性

図 11 にコフィン型熱疲労試験機による 200-900℃ で完全拘束の熱疲労試験結果を示す。参考のためにオーステナイト系の代表鋼である SUS 304 の結果もあわせて示した。高温疲労試験結果では強度レベルの高いものは高い疲労限界応力を示したが、熱疲労試験では同様な傾向は認められず、むしろ NSS 409 M 1, SUS 430 などの高温強度の低いものが若干長い熱疲労寿命を示し、その他のフェライト鋼はほとんど同一の熱疲労寿命となっている。フェライト系鋼とオーステナイト系の SUS 304 とを比較すると、いずれの鋼種も SUS 304 の約 2 倍以上の熱疲労寿命を示し、フェライト系鋼種がオーステナイト系鋼種よりも優れていることがわかる。この理由は、オーステナイト系鋼種がフェライト系鋼種に比べ約 1.7 倍の熱膨張率を有しており<sup>5)</sup>、熱疲労試験中の 1 回当たりの塑性変形量が大きく、結果的に熱疲労特性が劣ったものと考えられる。

写真 7 に熱疲労試験後の金属組織観察結果を示す。900℃ の高温疲労試験後の組織観察結果とはほぼ同様の結果となり、NSS 442 M 3, NSS EM1,

NSS 444 N は試験前に比べ、組織および結晶粒径の変化はほとんど認められなかったが、NSS 409 M 1 と NSS 430 M 3 は結晶粒の成長が観察された。一方、SUS 430 はマルテンサイト相の析出が認められた。

フェライト系鋼種のなかで NSS 409 M 1 と SUS 430 が長い熱疲労寿命となる理由については熱膨張率の違い<sup>6)</sup>や、相変態<sup>7)</sup>による引張りと圧

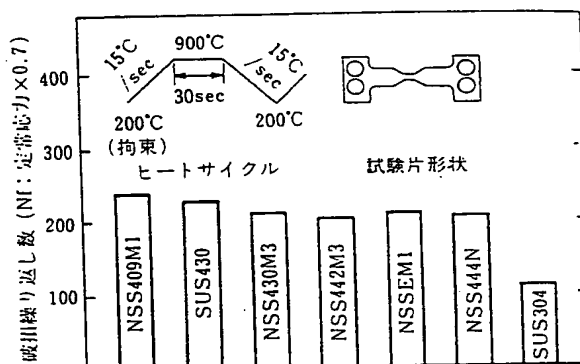


図 11 コフィン型熱疲労試験機による熱疲労特性 (200-900℃)  
Fig. 11 Number of cycles to failure by thermal fatigue in various stainless steels.

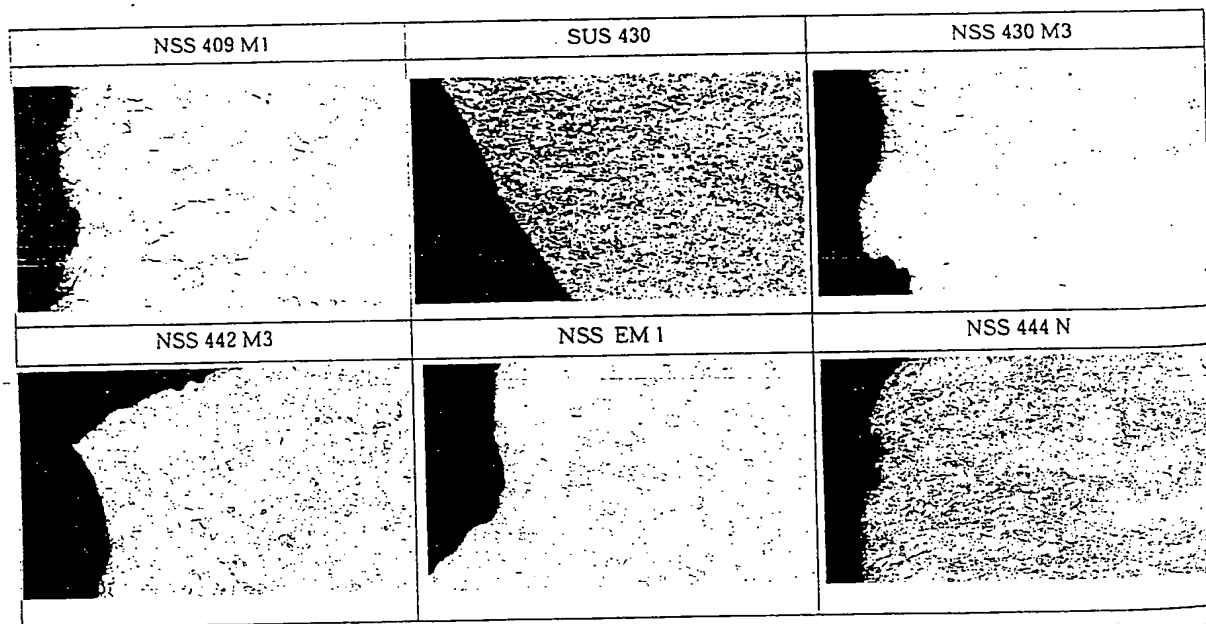


写真 7 熱疲労試験後の金属組織  
Photo. 7 Cracks on cross sections after thermal fatigue test.

縮時の応力緩和などが考えられるが、詳細については今後検討する必要がある。

#### 4. 結 言

フェライト系ステンレス鋼を耐熱用途に使用する場合の基礎となる耐熱データに関して系統的に検討した。供試材には、NSS 409 M 1 (11 % Cr-Ti), SUS 430 (16 % Cr), NSS 430 M 3 (17.5 % Cr-Ti-Mo), NSS 442 M 3 (19 % Cr-Cu-Nb), NSS EM 1 (19 % Cr-Mn-Nb) および NSS 444 N (19 % Cr-Nb-Mo) を用い、試験項目としては高温引張試験、高温酸化試験、高温疲労試験および熱疲労試験について実施した。以下に結果を要約して記す。

1) 連続酸化特性では NSS 409 M 1 および SUS 430 は 850 °C を超えると異常酸化を起こす。また、NSS 430 M 3, NSS 442 M 3 および NSS 444 N では 1000 °C まで異常酸化は起こさないものの、スケール剥離を生じた。一方、NSS EM 1 は 900 °C まで異常酸化およびスケール剥離を起こさず、良好な酸化特性を示した。

2) 繰り返し酸化特性では 900 °C までいずれの鋼種も異常酸化を起こさなかったものの、1000 °C では NSS 409 M 1 および SUS 430 が異常酸化を起こし、NSS 430 M 3, NSS 442 M 3 および NSS 444 N ではスケール剥離を生じた。一方、NSS EM 1 は 1000 °C においてもスケール剥離を起こさず、連続酸化同様、良好な酸化特性を示した。

3) 高温引張特性では 0.2 % 耐力および引張強さとも NSS 444 N がいずれの温度においても高い値を示し、ついで NSS 442 M 3 や NSS EM 1 などが高く、NSS 409 M 1 が最も低い値を示した。このことから、高温強度の改善には Cr, Mo および Nb などが有効と考えられる。

4) 高温疲労特性では 600 °C および 900 °C とも NSS 444 N が最も高い疲労限界応力を示し、NSS 409 M 1 が最も低い疲労限界応力を示した。この結果を同一温度の高温引張特性と比較すると、600 °C ではいずれの鋼種も疲労限界応力と引張強度がほぼ同じ値を示した。900 °C では NSS 409 M 1, SUS 430, NSS 442 M 3 および NSS

EM 1 が引張強度よりも低い疲労限界応力を示したのに対し、NSS 444 N および NSS 430 M 3 では引張強度よりも高い疲労限界応力を示した。

5) フェライト系ステンレス鋼の熱疲労特性はいずれも SUS 304 に比べ、約 2 倍の寿命を示した。フェライト系ステンレス鋼の中では NSS 409 M 1 および SUS 430 が比較的良好な熱疲労特性を示した。

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技術資料

## 各種フェライト系ステンレス鋼の耐熱性

中村定幸\* 平松直人\* 清水 勇\*\* 植松美博\*\*\*

## Heat Resisting Properties of Ferritic Stainless Steels

Sadayuki Nakamura, Naoto Hiramatsu, Isami Shimizu, Yoshihiro Uematsu

Synopsis :

Heat resisting properties such as high temperature oxidation, strength, fatigue and thermal fatigue were examined for various ferritic stainless steels. Steels used were NSS 409 M 1, SUS 430, NSS 430 M 3, NSS 442 M3, NSS EM 1 and NSS 444 N, and heat resisting properties were compared among these steels. The effect of alloying elements on heat resisting properties were also studied. The main results obtained are as follows:

- 1) Cr is very effective for improving high temperature oxidation resistance. In this study, NSS EM 1 exhibits the best properties of cyclic and isothermal oxidation resistance.
- 2) Cr, Nb and Mo are effective for improving high temperature strength. The best properties of high temperature strength and high temperature fatigue are obtained for NSS 444 N, followed by NSS EM 1 and NSS 442 M 3.
- 3) The property of thermal fatigue does not rely on its high temperature strength. All ferritic stainless steels exhibit good property of thermal fatigue comparing with austenitic stainless steel of SUS 304. This is due to the fact that ferritic stainless steels have lower thermal expansion than austenitic stainless steels.

## 1. 緒言

フェライト系ステンレス鋼は耐食性、加工性に優れ、かつオーステナイト系ステンレス鋼と比較して安価であるため、厨房用、温水器など耐食用途に広く使用されている。しかし、オーステナイト系ステンレス鋼に比べ高温強度が低く、耐熱用構造材料としてはあまり使用されていなかった。

最近、フェライト系ステンレス鋼の高温における表面酸化物の密着性を生かし、自動車排気ガス

浄化装置や各種の燃焼機器などで使用されるようになってきた<sup>1)</sup>。

これらの用途では、耐酸化性は勿論のこと、加熱・冷却にともなう熱応力、機械振動による高温疲労などが問題となる。フェライト系ステンレス鋼は熱膨張が小さく、かつ、熱伝導度が高いためオーステナイト系ステンレス鋼に比べ、優れた熱疲労特性を示す。したがって、フェライト系ステンレス鋼の欠点である高温酸化特性、高温引張り特性および高温疲労特性などの耐熱性を改善すれば、耐熱材料としても有望な鋼種となるものと考

\*鉄鋼研究所ステンレス・高合金研究部材料第一研究室 \*\*鉄鋼研究所ステンレス・高合金研究部製錬プロセス第3研究室 \*\*\*鉄鋼研究所ステンレス・高合金研究部材料第一研究室長

Table 1 Chemical Compositions

NSS444N Line 1 Elevated temperature fatigue; high temperature oxidation.  
NSS444N Line 2 Elevated temperature tensile strength; heat fatigue.

Table 4 Tensile properties of various ferritic steels at various elevated temperatures

0.2% proof stress; KGf / mm <sup>2</sup>	1.9
Pulling strength KGf/mm <sup>2</sup>	3.5
Stretch (%)	122.9
Diaphragm (stop) (%)	=100

Fig. 6 0.2% Proof stress and Tensile properties of various ferritic steels at various elevated temperatures

Vertical Axis: (bottom) Proof stress (kgf/mm<sup>2</sup>); (top) Tensile strength (kgf/mm<sup>2</sup>)

Horizontal axis: Temperature (°C)

Fig. 7 0.2% Proof stress and Tensile properties of various ferritic steels at Temperatures between 800 (°C) and 100 (°C)

Vertical Axis: (bottom) Proof stress (kgf/mm<sup>2</sup>); (top) Tensile strength (kgf/mm<sup>2</sup>)

Horizontal axis: Temperature (°C)

Fig. 8 Reduction and elongation of various ferritic steels at various temperatures

Vertical Axis: (bottom) Reduction (%); (top) Elongation (%)

Horizontal axis: Temperature (°C)